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ABSTRACT

The process of vaporization of niobium oxide, on which

no data have been reported in the literature, has been studied.

NbO was obtained by reducing niobium pentoxide with deoxygenated /691*

and dried hydrogen (refs. 1 and 2). According to spectral analysis data, the

purity of the initial Nb_2O_5 was 99.96 percent. The reduction was carried out

for 75 hours at 1250° at a hydrogen flow rate of 2.4 1/hr. The oxide obtained

was light gray in color. The relative amounts of niobium and oxygen in the

oxide, determined from the weight increase during roasting in air, corresponded

to the formula $NbO_{0.98}$. An X-ray powder pattern was also taken which agreed

completely with the reported data on the structure of NbO (refs. 3 and 4).

In our experiments, NbO was vaporized off a tungsten and an iridium strip

placed in the ion source of an MI-1305 mass spectrometer. In terms of the basic

circuit, the ion source was similar to the one described earlier (ref. 5). The

temperature was measured with a tungsten-rhenium thermocouple joined by spot

welding to the central portion of the strip. The thermocouple was calibrated

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* Numbers given in the margin indicate the pagination in the original foreign

text.

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at the High-Temperature Laboratory of VNIIM im. Mendeleyeva (All-Union Scientific Research Institute of Metrology) by means of a Class 1 optical pyrometer. The emf of the thermocouple was measured with a PP-1 potentiometer. The warming up of the mass-spectrometer chamber during the preparation of the experiments was carried out at a residual pressure of no more than $3-4 \cdot 10^{-5}$ mm Hg.

The table lists average results of mass spectrum measurements for a temperature of the evaporator strip of $1630^{\circ}C$, an electron emission current of 1.5 mA, and two ionizing potentials, 50 and 15 V.

It is well known that ionization by electron impact produces, in addition to the "basic" ions corresponding to neutral molecules, the so-called "fragment" ions arising from dissociative ionization. In our case, the NbO_2^+ ion is "basic," since the spectrum did not show any heavier masses from which the NbO_2^+ fragment could have been formed.

In order to determine the origin of NbO^+ ions, we estimated their appearance potential by recording the ion current of NbO^+ as a function of the ionizing potential. To calibrate the potential scale, the appearance potentials of the ions H_2O^+, Ar^+ and Hg^+ were measured. The results are shown in figure 1, from which it is apparent that Curve 5 has an inflection corresponding to the instant

MASS SPECTRUM OF VAPORS OVER NIOBIUM OXIDE.

Ion	Relative intensity at potential (V) of	
	50	15
Nb^+	0.28	-
NbO^+	0.96	0.65
NbO_2^+	1.0	1.0

Figure 1. Appearance potential of the

ions: 1, Hg^+, 2; H_2O^+; 3, Ar^+; 4, NbO_2^+;

5, NbO^+; 6, Nb^+.

at which the dissociative ionization of NbO_2 begins (segment BC). Segment AB

characterizes the ionization of NbO molecules. The appearance potential of

NbO^+ ions may be estimated at 10.5 eV.

The complete absence of Nb^+ ions at an ionizing potential of 15 V indicates

that they   formed by dissociative ionization (Curve 6). Hence, we observed

two types of ions corresponding to the neutral molecules NbO_2 and NbO, which

were present in pairs. This leads to the assumption that in addition to the

vaporization of NbO, a disproportionation takes place as follows

$$2[NBO]_s \rightarrow [Nb]_s + (NbO_2)_{gas}.$$
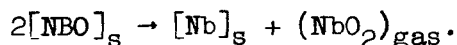
We measured the temperature dependence of the ion currents of NbO_2^+, NbO^+

and Nb^+. Results of these measurements for the $1500-1650°$ temperature interval,

expressed graphically as the function $\log (I^+ \cdot T) = f(1/T)$, are shown in figure 2.

The heat of sublimation of NbO_2, found from the slope of Curve 1, corresponds

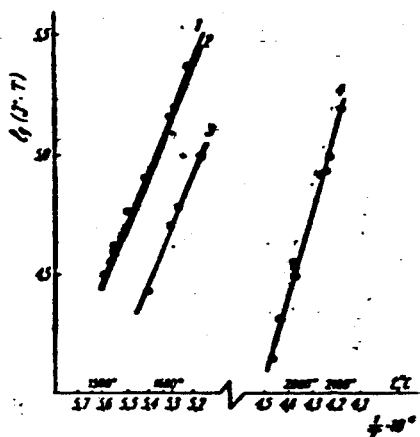to 140 ± 3 kcal/mole, which is in agreement with the heat of sublimation of

Figure 2. Temperature dependence of ion currents: 1, NbO^+; 2, NbO^+; 3, Nb^+; 4, Nb^+ (at temperatures above 1900°C).

niobium dioxide which we determined earlier (ref. 6). The heat of sublimation of NbO determined from the slope of Curve 2 is equal to 138 ± 3 kcal/mole.

We estimated the comparative value of the vapor pressures of NbO_2 and NbO at 1650° on the basis of the ratio of ion currents of NbO_2^+ and NbO^+. The value of the current of NbO^+ was first corrected by using the current ratio for the "basic" and "fragment" ions obtained earlier for pure NbO_2: $I_{NbO_2^+} : I_{NbO^+} = 1 : 0.38$

The effective ionization cross sections of the NbO_2 and NbO molecules, borrowed from Otvos and Stevenson (ref. 7) are :

$$\frac{\sigma_{iNbO_2}}{\sigma_{iNbO}} = \frac{64.2}{60.9} = 1.05.$$

With the indicated corrections, we obtain

$$P_{NbO_2} : P_{NbO} = 1 : 0.57.$$

In order to make sure that the disproportionation of NbO occurs simultaneously with its vaporization under our experimental conditions, we kept

4

an evaporator strip with a sample in the mass spectrometer at 1650° while continuously monitoring the ion currents of NbO_2^+ and NbO^+. These currents declined as the substance evaporated, and after a while they disappeared completely. A dense layer of sintered metallic niobium was observed on the strip. When the strip was heated to 1950°, no ions corresponding to niobium or its oxides were observed. Beginning at 1950°, only Nb^+ ions appeared. The temperature dependence of the ion current of Nb^+ was measured in the 1970-2120°C range and is graphically represented in the function $\log (\overset{+}{I} \cdot T) = f(1/T)$ in figure 2 (Curve 4). Calculated from the slope of the curve, the heat of sublimation of metallic niobium is 172 ± 5 kcal/g-at.

It should be noted that a search for WO^+, WO_2^+ and WO_3^+ ions in work with the tungsten evaporator strip gave negative results. The absence of the reducing action of tungsten was also confirmed by the identity of the mass spectra during evaporation of NbO off tungsten and iridium strips. On rapid heating of the evaporator to the working temperature, no increase in the currents of O_2^+ and O^+, whose small "background" always exists in the mass spectrometer, was observed.

SUMMARY

1. The composition of the vapor over niobium monoxide was studied mass-spectrometrically for the first time.

2. It was shown that the competing processes of evaporation and disproportionation occur simultaneously during the evaporation of NbO.

3. The heat of sublimation of NbO in the 1500-1650° range is equal to 138 ± 3 kcal/mole.

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